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(71) Anmelder (*für alle Bestimmungsstaaten ausser US*): DYNEON GMBH [DE/DE]; D-84504 Burgkirchen (DE).

(72) Erfinder; und
(75) Erfinder/Anmelder (*nur für US*): BLÄDEL, Hermann [DE/DE]; Mühlbachstrasse 96, D-84547 Emmerting (DE). HINTZER, Klaus [DE/DE]; Lindenstrasse 16a, D-84556 Kastl (DE). LÖHR, Gernot [DE/DE]; Schneibsteinstrasse 6, D-84508 Burgkirchen (DE). SCHWERTFEGER, Werner [DE/DE]; Oberer Grasweg 16c, D-84503 Altötting (DE). SULZBACH, Reinhard, Albert [DE/DE]; Kammererstrasse 10, D-84489 Burghausen (DE).

(74) Gemeinsamer Vertreter: DYNEON GMBH; D-84504 Burgkirchen (DE).

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(54) Title: AQUEOUS DISPERSIONS OF FLUOROPOLYMERS

(54) Bezeichnung: WÄSSRIGE DISPERSIONEN VON FLUORPOLYMEREN

(57) Abstract

Emulsifiers containing fluorine can be separated out of fluoropolymer solutions by adding a non-ionic emulsifier to the dispersion, by separating the emulsifier which contains fluorine by bringing the same into contact with an anion exchanger, and by separating the dispersion from the anion exchanger. The obtained dispersions can be concentrated and can be used for coating applications.

(57) Zusammenfassung

Fluorhaltige Emulgatoren können aus Fluorpolymerdispersionen abgetrennt werden, indem man die Dispersion mit einem nichtionischen Emulgator versetzt, den fluorhaltigen Emulgator durch Inberührungbringen mit einem Anionenaustauscher abtrennt und die Dispersion vom Anionenaustauscher abtrennt. Die erhaltenen Dispersionen können aufkonzentriert und für Beschichtungsanwendungen verwendet werden.

Aqueous dispersions of fluoropolymers

The invention is concerned with aqueous dispersions of fluoropolymers being essentially free of fluorine-containing emulsifiers, a process for making such dispersions and their use. “Essentially free” means a content of less than 100 ppm, preferably less than 50 ppm, especially less than 25 ppm and in particular less than 5 ppm.

Polyfluoroethylene-dispersions find broad applications in the coating industry due to the unique performance of the coatings e.g. antistickiness, good weatherability, and noninflammability. They are mainly used for coating kitchen ware, chemical apparatures and glass fabrics. In many such applications, the dispersions are applied at relatively high solid contents, e.g., up to 70 weight-%. These concentrated dispersions are prevailingly colloid chemically stabilized by nonionic emulsifiers such as alkyl aryl polyethoxy alcohols and alkyl polyethoxy alcohols.

There are basically two different polymerization processes for making fluoropolymers, namely the suspension polymerization leading to a granulat polymer and, on the other hand, the so-called emulsion polymerization leading to an aqueous colloidal dispersion. This invention concerns the emulsion polymerization, the so-obtained dispersions and their use.

The manufacturing of such dispersions involves basically two processing steps the polymerization and upconcentration.

By the aqueous emulsion polymerization process, there can be produced firstly to non-melt processible homopolymers, e. g. PTFE, secondly to “modified” polymers, e. g. a polymer containing more than about 99 mol% of tetrafluoroethylene (TFE) and

only such a small amount of comonomer(s) to render the product still not processible from the melt, thirdly, low molecular weight "micro powder" dispersions which are processible from the melt and fourthly to copolymers, such as fluorothermoplasts or fluoroelastomers. Fluorothermoplasts include copolymers consisting predominantly of TFE and an amount of one or more comonomer(s), e. g. 1 to 50, preferably 1 to 10 mol%, so that the product is processible from the melt. Common fluoromonomers are, besides TFE, vinylidene fluoride (VDF), other fluorinated olefins, such as chloro-trifluoroethylene (CTFE), especially perfluorinated olefins of 2 to 8 carbon atoms, e. g., hexafluoropropene (HFP), fluorinated ethers, especially perfluorinated vinyl-alkylethers with alkyls of 1 to 6 carbon atoms; e. g. perfluoro-(n-propyl-vinyl)-ether (PPVE). Useful comonomers can also be nonfluorinated olefins, e. g. ethylene and propylene. The so obtained dispersions of polymers, which may be melt-processible or not, usually have solids content of 15 to 30 weight-%. Therefore, for obtaining the above-mentioned high solids content for application as a coating, and – advantageously – also for storing and transportation the solids content has to be increased by upconcentration. Practiced, for example, are the thermal upconcentration as described in US-A 3 316 201, the decantation (US-A 3 037 953) and the ultrafiltration (US-A 4 369 266).

The known emulsion polymerization is carried out mostly within a pressure range of 5 to 30 bars and within a temperature range of 5 to 100 °C as described e.g. in EP-B 30 663. The polymerization process to make PTFE-dispersions is essentially the same as the known process to make fine resin powders, so called paste ware (US-A 3 142 665). The polymerization process to produce copolymers such as fluorothermoplast dispersions is the same process as to produce these materials applied as melt pellets.

All these emulsion polymerizations have in common that they need an emulsifier which does not interfere the polymerization by chain transfer reaction. These emulsifiers are called non-telogenic emulsifiers (US-A 2 559 752). Predominantly, perfluorooctanoic (PFOA) acids (such as n-PFOA, CAS No. 335-67-1) are used as

ammonium and/or alkali salts. When in the following text "PFOA" is used for short it is to be understood that other fluorinated emulsifiers are not excluded. The content of this emulsifier usually ranges from 0,02 to 1 weight-% with respect to the polymer.

Occasionally other fluoroemulsifiers are used. For example EP-A 822 175 describes the use of salts of CH_2-containing fluorocarboxylic acids for the emulsion polymerization of TFE. WO-A 97/08214 discloses the use of 2-perfluorohexyl ethanesulfonic acid or salts for TFE polymerization.

Still further fluorinated emulsifiers are described in US-A 2 559 752. However, these emulsifiers are not commonly used because of their low volatility. These chemicals may result in discoloration of the end products at high processing temperatures.

One of the biggest advantages of PFOA is its high volatility. PFOA is a very powerful emulsifier and due to its inertness during the polymerization is practically indispensable. However, PFOA is biologically non degradable and recently is scrutinized as a health hazard to the environment.

However, it is known to remove PFOA from waste gases (EP-B 731 081) and, furthermore, advantageous processes have been proposed from waste water (US-A 4 282 162 and yet unpublished German Patent Applications 198 24 614.5 and 198 24 615.3 filed June 2,1998).

In the above mentioned upconcentration technologies the PFOA largely stays with the polymer dispersion, even at the ultrafiltration and the decantation even with a hundred fold excess of the nonionic emulsifier.

For instance at the ultrafiltration as described in US-A 4 369 266, about 30 % of the original PFOA content stays with the commercial dispersions. In special cases the remaining PFOA content can be reduced to less than 10 % but the process is generally economically not feasible: To achieve such a reduction one has to replenish

the water and a nonionic emulsifier to the dispersion to be upconcentrated. This makes the run times unacceptably long.

During subsequent use of these dispersions, the PFOA may be released to the environment, e.g. via the unavoidable waste-water for cleaning the equipment and via an aerosol into the atmosphere. The latter release is enhanced at the making of the coatings since PFOA and its ammonium salt are very volatile. Furthermore, at the normally used sintering temperatures of 350 to 450 °C PFOA and its salts are decomposed by decarboxylation to fluorocarbons. These chemicals have a high warm up potential for the climate ("green house effect").

The present invention provides high solid dispersions essentially free of PFOA. In this invention, "essentially free" means a content of less than 100 ppm, preferably less than 50 ppm, especially less than 25 ppm and in particular less than 5 ppm. These values are based on the entire dispersion, and not just the solids content. This is achieved by removal of fluorinated emulsifiers, e.g. PFOA, from fluoropolymer dispersions, such as PTFE, fluorothermoplast or fluoroelastomer dispersions, via anion exchange, namely by adding a nonionic emulsifier to the fluoropolymer dispersion and contacting this stabilized dispersion with a basic anion exchanger. This process works without jamming or clogging the ion exchange bed by coagulated latex particles. The resulting dispersion may optionally be upconcentrated

Fluoropolymer dispersions useful in this inventions include dispersions of homopolymers and copolymers of one or more fluorinated monomers, such as TFE, VDF or CTFE or other fluorinated olefins of 2 to 8 carbon atoms, perfluorinated olefins of 2 to 8 carbon atoms, e.g., HFP, fluorinated ethers, especially perfluorinated vinyl-alkyl ethers with alkyls of 1 to 6 carbon atoms, such as perfluoro-(n-propyl-vinyl) ether and perfluoro-(methyl-vinyl) ether. Useful comonomers also include non-fluorinated olefins, such as ethylene or propylene. This invention is intended to include such dispersions whether the resulting fluoropolymer is melt-processible or not.

The latex particles usually have a submicroscopic diameter of less than 400 nm and preferably between 40 – 400 nm. Smaller particle sizes may be obtained by so-called "micro-emulsion polymerization." The latex particles are anionically stabilized in the sense of colloid chemistry. The anionic stabilization is provided by anionic endgroups, mostly COOH-groups, and by the anionic emulsifier such as PFOA. Such anionically stabilized dispersions coagulate rapidly in an anion exchange bed and thus jam the ion exchange bed. The reason for that is the break down of the electrical double layer at the ion exchange sites. Therefore the treatment of an anionically stabilized dispersion with an anion exchanger is considered to be technically not feasible, in particular for higher concentrations.

The impairing or clogging of an ion exchange bed is already observed at concentrations 1000 times lower than those of the raw polymer dispersions, that is the dispersion after polymerization.

Helpful for the choice of a useful ion exchanger is the observation that the pKa value of the acid corresponding to the counterion of the anion exchanger has to be higher than the pKa value of the anionic endgroups of the polymer. Preferably, the anion exchanger has a counterion corresponding to an acid with a pKa value of at least 3.

In contrast, coagulation is observed on the long term if the anion exchanger is in the SO_4^{-2} or Cl^- form even with dispersions of copolymers of TFE with HFP, called "FEP", and of TFE with PPVE, called "PFA". These copolymers both have strongly acidic endgroups. The formation of such endgroups is explained in "Modern Fluoropolymers", John Scheirs (Editor), John Wiley & Sons, Chichester (1997), pages 227 to 288, 244. The jamming or clogging of ion exchange beds when processing TFE-ethylene or vinylidene fluoride copolymer dispersions occurs under such conditions almost instantly.

Therefore, at the outset, the anion exchange is performed in an essentially basic environment. Preferably, the ion exchange resin is transformed to the OH^- form, but

anions like fluoride or oxalate corresponding to weak acids can also be used. These anions are generally present in the dispersion from the polymerization recipe.

The specific basicity of the anion exchanger used is not very critical. Strongly basic resins are preferred due to the observed higher efficiency in removing PFOA. The effective removal of PFOA from the dispersions depends on the ion exchange conditions. Weakly basic ion exchange resins show earlier PFOA break through. The same is true for higher flow rates.

The flow rate is not very critical, standard flow rates can be used. The flow can be upward or downward.

The ion exchange process can also be carried out as a batch process by mildly stirring the dispersion with the ion exchange resin in a vessel. After this treatment the dispersion is isolated by filtration. Use of this invention will minimize coagulation during a batch process.

Non ionic emulsifiers are described in detail in "Nonionic Surfactants edited by M. J. Schick, Marcel Dekker, Inc., New York 1967".

The choice of the nonionic emulsifier is not critical either. Alkyl aryl polyethoxy alcohols, alkyl polyethoxy alcohols, or any other non ionic emulsifier can be used. This is a big advantage since the removal of PFOA from commercial dispersions leaves the formulation of the applied dispersions essentially unchanged.

No differences could be observed using non ionic surfactants such as alkyl aryl polyethoxy alcohol type, e.g., Triton™ X100, or alkyl polyethoxy alcohol type, e.g., GENAPOL™ X 080, with respect to effectiveness of the PFOA removal, flow rates, or jamming of the ion exchanger bed.

The removal of PFOA is preferably carried out with raw dispersions from the polymerization. Such dispersions generally have a solid content of 15 to 30 weight-% to which is added sufficient non-ionic emulsifier to provide dispersion stability during subsequent processing, such as upconcentration. A sufficient quantity of non-ionic emulsifier generally means from 0.5 to 15 weight-% and preferably from 1 to 5 weight-%. These percentages are based upon the solids content of the dispersion. After removal of the PFOA, the dispersions may be upconcentrated using conventional procedures, such as ultrafiltration or thermal upconcentration. It is advantageous that the concentration of the non-ionic emulsifier in the final product is not much higher than in comparable commercial products. The absence of PFOA at these processes is not negatively affecting the upconcentration, that is, not more coagulum is formed than in presence of PFOA at the thermal upconcentration and the ultrafiltration.

The removing of PFOA via anion exchange can also be carried out with already upconcentrated dispersions with a solids content of up to 70 weight-%. However, due to the higher viscosity and density of such dispersions the process is technically more cumbersome. In this case the ion exchange is preferably driven upstream to avoid difficulties due to the floating of the ion exchange bed. Mostly the high viscosity does not permit high flow rates. For such high solid dispersions the batch process appears to be more advantageous.

The removal of PFOA is carried out by adding typically 1 to 5 weight-% nonionic emulsifier to the dispersion under mild agitation conditions and passing over the anion exchanger. The anion exchanger may be preconditioned with a solution of nonionic emulsifier as used with the dispersion to be exchanged. The anion exchange resin is preferably brought into the OH^- form. This is accomplished by contacting the anion exchange resin with a NaOH solution.

Usually dispersions are used for the ion exchange process without adjusting the pH value but the pH value may be increased to enhance the colloidal stability of the

dispersion by adding a base like aqueous ammonia or sodium hydroxide solution. A pH value in the range of 7 to 9 is sufficient. The increased pH value does not affect very much the efficiency of the removal of PFOA. This is believed to be due to the fact that PFOA is not only exchanged but also strongly absorbed on the ion exchange resin.

Subsequently the ion exchanged dispersions are subjected to upconcentration, preferably using thermal upconcentration or ultrafiltration. No impairing of these processes are observed. Furthermore the end user processing and end use properties for such dispersions according to this invention are not changed.

The anion exchange process in the presence of a non ionic emulsifier without jamming the ion exchange bed can be successfully used for the removal of any other anionic emulsifier used in any polymerisation process.

This process may also be used for any fluoropolymer raw dispersions, such as, for example, dispersions of PFA, FEP, THV (THV is a terpolymer of TFE, HFP VDF), ET (ET is a copolymer of TFE and ethylene), TFE/P (a copolymer of TFE and propylene), copolymers of VDF and HFP as well as homopolymers or copolymers comprising other fluorinated olefins or vinyl ethers. These polymers are described in detail in “Modern Fluoropolymers” cited above.

The work up procedure as disclosed in US-A 5 463 021 describes inter alia, a treatment of THV raw dispersions via an ion exchange process as one work up step. However, this is a cationic exchange process to remove the manganese ions originated from the permanganate used as polymerization initiator. During the cationic exchange process the stabilizing electrical double layer is not affected because the latex particles are anionically stabilized.

The invention is illustrated by the following examples.

Experimental details:

All percentages are by weight unless otherwise stated.

Determination of PFOA

The PFOA content of the anion exchanged dispersion may be quantitatively analyzed by using the method described in "Encyclopedia of Industrial Chemistry Analysis", Vol. 1, pages 339 to 340, Interscience Publishers, New York, NY, 1971 and in EP-A 194 690. Another method used is the conversion of the PFOA to its methyl ester and analyzing the ester content by gas chromatography using an internal standard. The detection limit for PFOA for the latter method is 5 ppm. The latter method was used in the following examples

Anion exchange

Standard equipment was used. The dimensions of the column were 5 x 50 cm. AMBERLITE™ IRA 402 with a capacity of 1.2 meq/ml as strong basic anion exchange resin was used (AMBERLITE is a Trademark of Rohm & Haas). The bed volume was usually 400 ml. The ion exchanger was brought into the OH^- form with NaOH solution. The exchanger was preconditioned with a 5%-solution of the non ionic emulsifier. The ion exchange was carried out at room temperature. The experiments were performed at different flow rates as given in Table 1. The non ionic emulsifier was added as a 10 % concentrated solution to the dispersions. The content was varied as given in Table 1. The values are based on the polymer content. The technical feasibility of this process is considered to be accomplished if at least 5 % of the theoretical capacity of the ion exchange resin supplied is consumed by the PFOA containing dispersion without jamming the bed and without break through of PFOA.

The nonionic surfactants applied are:

NIS 1: octyl phenoxy polyethoxy ethanol (commercial product TRITON™ X 100, TRITON is a Trademark of Union Carbide Corp.).

NIS 2: ethoxylate of a long-chain alkanol (commercial product GENAPOL™ X 080, GENAPOL is a Trademark of Hoechst AG).

Examples 1 to 7

All experiments were carried out with AMBERLITE IRA 402 in the OH^- form. Preconditioning of the anion exchange resin with an aqueous solution of the non ionic surfactant was changed as indicated in Table 1.

The fluoropolymer dispersion was obtained by homo-polymerization of TFE according to EP-B 30 663. The solid content of the raw dispersion used is about 20 %, and the average particle size is about 200 to 240 nm. The pH value is 7. The amount and the type of the non ionic emulsifier added to the raw dispersion was changed as indicated in Table 1.

The PFOA content of the dispersion is about 0.13 weight-% (amounting to 3.14 mmol/kg dispersion). This corresponds to 2.7 ml of ion exchange resin per kg of raw dispersion. Example 3 shows that 54 ml of the total volume of 400 ml ion exchange resin are used. Thus, the provided ion exchange capacity was more than 5 times in excess for all examples.

The experimental details in Table 1 show different flow rates. During a given experiment no changes in the flow rate were observed. This is an indication of the absence of jamming of the ion exchange bed. The run time of the experiments was up to 67 h without interruption. All the examples result in dispersions with PFOA contents of less than 5 ppm, the analytical detection limit of the method used.

TABLE 1

Example No.	1	2	3	4	5	6	7
Ion exchange resin, ml	400 ml	400 ml	400 ml	4 parallel columns 400 ml each	4 parallel columns 400 ml each	400 ml	400 ml
Ion exchange resin conditioned with an aqueous solution of	1 weight-% NIS 1	5 weight-% NIS 1	3 weight-% NIS 1	5 weight-% NIS 1	5 weight-% NIS 2	5 weight-% NIS 2	1 weight-% NIS 2
Raw dispersion:							
Solid content of	22.7 %	22.6 %	22.7 %	22.7 %	22.5 %	23%	22.8 %
PFOA content	0.132 %	0.130 %	0.132 %	0.136 %	0.138 %	0.138 %	0.136 %
Raw dispersion							
Stabilized with *)	1% NIS 1	3% NIS 1	4% NIS 1	5% NIS 1	5% NIS 2	4% NIS 2	1% NIS 2
Amount passed through	5 kg	19 kg	20 kg	40 kg	50 kg	18 kg	8 kg
Flow rate	0.5 l/h	0.6 l/h	0.3 l/h	0.6 l/h	0.6 l/h	0.6 l/h	0.5 l/h
Run time	10 h	35 h	67 h	17 h	21 h	30 h	16 h
Jamming yes/no	No	no	no	no	no	no	no
Ion exchanged dispersion							
PFOA content	<5 ppm	<5 ppm	<5 ppm	<5 ppm	<5 ppm	<5 ppm	<5 ppm
	*) based on solid content of the dispersion						

Example 8

800 ml of AMBERLITE IRA 402 (OH^- form, preconditioned with a 5%-solution of NIS 1) was slowly added to a stirred vessel containing 20 liters of dispersion similar to that used in examples 1 to 7, but upconcentrated by ultrafiltration (solid content: 52.5 %, PFOA content: 0.065 %, NIS 1 content: 5 % based on polymer content). After mild stirring for 8 h at room temperature the anion exchanger was filtered off and the PFOA content of the dispersion was analyzed resulting in less than 5 ppm PFOA.

Example 9

The same procedure as for examples 1 to 7 was used for purification of a PFA raw dispersion. 400 ml of AMBERLITE IRA 402 (OH^- form, preconditioned with 1%-solution of NIS 2) were used. The PFA dispersion (1500 ml, solid content 20 %) was stabilized with 5 weight-% of NIS 2 based on the solid content of the dispersion. This dispersion contained 0.066 weight-% of PFOA and showed a pH value of 4. The dispersion was passed over the anion exchanger bed with a flow rate of 100 ml/h. This corresponds to a run time of 15 h. No jamming of the bed was observed and the resulting dispersion showed a PFOA content of <5 ppm.

Example 10

Example 9 was repeated using a FEP raw dispersion (solid content 20 weight-%, PFOA content 0.08 weight-%) stabilized with 5 weight-% of NIS 2. The ion exchange process resulted in a FEP dispersion containing <5 ppm of PFOA. No jamming of the bed was observed.

Example 11

Example 9 was repeated but with a THV dispersion having a solid content of 20 % and a average particle size of 80 nm. Before subjecting the dispersion to the anion exchange it was treated with a cation exchange resin as described in US-A 5 463 021. The anion exchange process resulted in a THV dispersion containing <5 ppm of PFOA and no jamming of the bed was observed.

Claims:

1. Aqueous fluoropolymer dispersion, being essentially free of fluorine-containing emulsifier.

2. Dispersion according to claim 1, containing less than 100, preferably less than 50, especially less than 25 and particularly less than 5 ppm of fluorine-containing emulsifier.

3. Dispersion according to claims 1 or 2, characterized in that the fluoropolymer is a polymer of tetrafluoroethylene.

4. Dispersion according to claim 3, characterized in that the polymer contains at least one monomer selected from the group consisting of fluorinated olefins of 2 to 8 carbon atoms and fluorinated vinyl-alkyl ethers with an alkyl of 1 to 6 carbon atoms.

5. Dispersion according to claim 4, characterized in that the fluorinated olefin and ether is perfluorinated.

6. Dispersion according to claim 4, characterized in that the fluorinated olefin is hexafluoropropene and/or vinylidene fluoride.

7. Dispersion according to claim 5, characterized in that the ether is perfluoro-(n-propyl-vinyl) ether or perfluoro-(methyl-vinyl) ether.

8. Dispersion according to claim 3, characterized in that the polymer contains 90 to 100 mol% tetrafluoroethylene.

9. Dispersion according to claims 1 or 2, characterized in that the fluoropolymer comprises one or more fluorinated monomers, with the proviso that none of the

monomers are tetrafluoroethylene.

10. A process for removing fluorine-containing emulsifier from an aqueous fluoropolymer dispersion which comprises adding to the said dispersion an effective amount of a nonionic emulsifier to stabilize the dispersion, contacting this stabilized dispersion with an effective amount of an anion exchanger to essentially remove fluorine-containing emulsifier and separating the dispersion from the anion exchanger and optionally, subjecting the so-obtained dispersion to upconcentration.

11. The process as claimed in claim 10, characterized in that the solids content of the said dispersion is 10 to 70 weight-%.

12. The process as claimed in claim 11, characterized in that the solids content is 15 to 30 weight-%.

13. The process as claimed in one or more of claims 10 to 12, characterized in that 0.5 to 15 % by weight of nonionic emulsifier are added, based on the weight of the solids content of the dispersion.

14. The process as claimed in claim 13, characterized in that the nonionic emulsifier concentration is preferably 1 to 5 % of the solids content.

15. The process as claimed in one or more of claims 10 to 14, characterized in that the anion exchanger has a counterion corresponding to an acid with a pKa value of at least 3.

16. The process as claimed in one or more of claims 10 to 15, characterized in that the anion exchanger is used in the hydroxyl form.

Abstract

Fluorine-containing emulsifiers can be removed from fluoropolymer dispersions by adding to the dispersion a non ionic emulsifier, removing the fluorine-containing emulsifier by contact with an anion exchanger and separating the dispersion from the anion exchanger. The resulting dispersions can be upconcentrated and used for coating applications.